Offprint

Pore Conductivity and Streaming Potential in Charged Capillary Tubes with Concentration Dependent Pore Wall Charge

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Registration Number 532

Abstract

The pore conductivity and the streaming potential in charged capillary tubes with concentration dependent pore wall charge have been theoretically analysed. The charge is assumed to be due to ion adsorption in presence of electrolyte solutions, and the theoretical model is based on two simplified forms of the Poisson-Boltzmann equation. Comparison between theory and experimental data from the literature (G. B. Westermann-Clark and J. Anderson, J. Electrochem. Soc., 130 (1983), 839) gives a reasonable agreement for the case of charged membranes inmersed in aqueous alkali chloride solutions, and shows that the *same* adsorption isotherm can describe *both* the pore conductivity and the streaming potential over a wide bulk concentration range. A "patched" Freundlich type relationship is introduced for the charge adsorbed to the pore wall in order to incorporate the Freundlich adsorption isotherm characteristics for small values of bulk electrolyte concentration as well as the Langmuir isotherm ones for high values of this concentration.

1. Introduction

Studies of transport processes in charged membranes have usually considered the membrane structure as composed by an array of paralell capillary tubes carrying a uniform pore wall charge (see Refs. [1–3] and references therein). The theoretical foundations of this model are based on the Gouy-Chapman approach for the electrical double layer at the pore surface, the Nernst-Planck equation for ion fluxes, and the Navier-Stokes equation for describing the solution flow through the capillary tubes. Pintauro and Verbrugge [3] have recently extended this theory by including microscopic events that require molecular-level models. Although their treatment is restricted to a membrane under *equilibrium*

conditions, it is clear that consideration of molecular-level models should be of great interest in the case of small pore dimensions.

A key parameter of the charged capillary membrane models is the immobile, uniform charge density at the pore wall, σ. Transport parameters like the pore conductivity, the concentration and streaming potentials, the membrane selectivity, and the solute permeability of the pore critically depend on this charge. One of the most usual simplifications contained in the model is to assume the charge density σ to be *constant*. A series of studies have shown that σ is not constant, but depends instead on the experimental conditions considered [1, 2, 4–7]. This question seems to have received little attention in the literature. Indeed, the simultaneous dependence of σ on the amount of polyelectrolyte introduced [1], the bulk electrolyte concentration [1, 2, 4–7], the pH of the solution [2] and the solvent properties (ion adsorption may be inhibited by some solvents [4]) make it very difficult to incorporate all these effects in a particular equation for σ. Note also that the integration of the set of non-linear differential equations ruling the problem is a formidable task even when σ is assumed to be constant [2, 7].

In a recent paper [8] we included the dependence of σ on the bulk electrolyte concentration, c, by employing a Freundlich adsorption isotherm [9]. We showed that the introduction of this particular relationship for the change of σ with c improved significantly the agreement between theory and experiment in the case of the pore conductivity, κ, measurements, as noted previously by Westermann-Clark and Anderson [2], and Martínez *et al.* [6]. (These authors solved numerically the equations of the model assuming a constant value for σ, and comparison between theory and experiment required the introduction of a set of theoretical curves of parameter σ in order to account for the observed values of the pore conductivity at different concentrations.) However, a fundamental question remained unsolved there [8]: that of the validity of the same adsorption isotherm for describing not only the pore conductivity but also the measured streaming potential, v. The study of this question is of interest, since pore conductivity and streaming potential are two independent phenomena in a phenomenological sense, and hence each one gives an independent estimate of σ as a double layer property. Here we will modify the relationship for σ introduced in Ref. [8] in order to account for both, the observed κ and v values. To carry out such an analysis, the experimental results supplied by Westermann-Clark and Anderson [2] will be considered. These results were obtained under carefully controlled experimental conditions: for large-pore membranes certain time and pH requirements were met in order to ensure a stable wall charge, and the pH-independent value of σ was reported to be negative for aqueous electrolytes with monovalent cations, its magnitude increasing with the chloride ion concentration. These facts will allow us to account only for the bulk concentration dependence of σ, which makes the problem much simpler. Note that this condition is not very restrictive since most of the experimental analyses from the literature refer to aqueous electrolytes, and have been conducted under nearly constant pH values.

2. Formulation of the problem

A. Solutions to the Poisson-Boltzmann (P-B) equation

The main assumptions included in the charge capillary model can be found elsewhere [1–3]. Our theoretical treatment is based on two simplified forms of the Poisson-Boltzmann equation. They correspond to the limits of "large" and "small" (a/λ) values, where a is the pore radius and λ the Debye length. Altough these limiting cases lead to two approximated solutions of the general problem, both have theoretical and practical interest [5, 8, 10]. In the limit of $(a/\lambda) \gg 1$, the $P - B$ equation can be linearized, and the well-known [8] final solutions is

$$\Psi(r/\lambda; x) = \frac{\sigma\lambda}{\varepsilon} \frac{I_0(r/\lambda)}{I_1(a/\lambda)}, \tag{1}$$

where Ψ is the local electric potential, $I_j (j = 0, 1)$ is the modified Bessel function of jth order, r and x are the radial and axial coordinates, respectively, and λ is the Debye length defined as

$$\lambda(x) = \left[\varepsilon RT/F^2 \sum_i z_i^2 \bar{c}_i(x) \right]^{1/2}. \tag{2}$$

In equation (2), ε stands for the fluid dielectric constant, F is the Faraday constant, R is the gas constant, and T is the absolute temperature, while z_i and $\bar{c}_i$ denote the charge number and the axial molar concentration of the ith ion within the pore, respectively. In the limiting case considered, $\bar{c}_i \approx c$, being this concentration the same in the two bulk solutions for the pore conductivity and streaming potential measurements.

For the other limiting case of the $P - B$ equation, which corresponds to $(a/\lambda) \leq 1$, we have to solve the full, non-linearized $P - B$ equation under conditions of total coion exclusion (the limit in which only those ions of charge opposite to that of the pore wall would fill in the pore). In this case it is well-known [1, 8, 10] that an analytical solution can be found. In our case this takes the form:

$$\Psi(r/\lambda) = \frac{2RT}{F} \ln \left[1 - \frac{F^2 \bar{c} r^2}{8\varepsilon RT} \right], \tag{3}$$

where now the electrolyte concentration in the cylindrical pore axis, $\bar{c}$, is related to σ by the equation:

$$\bar{c} = - \frac{2\sigma}{aF(1 - p)}, \quad p \equiv \frac{Fa\sigma}{4\varepsilon RT}. \tag{4}$$

Equation (4) can be readily obtained by imposing that the total charge in the pore due to the presence of coions has to be equal to the pore wall charge (local electroneutrality condition).

Equations (1) and (3) are only two approximated solutions to the full $P - B$ equation. However, previous analyses have shown that the potential profiles so obtained deviate only slightly from that obtained by numerical solution of the original $P - B$ equation (see [10] and references therein). Thus, we will employ (1) and (3) as a first approximation to the problem.

B. Concentration dependent pore wall charge

In absence of charged polyelectrolytes in the bulk solutions, the large-pore observations of Ref. [2] indentified a series of experimental conditions influencing the pore wall charge σ. As stated in the Introduction, we consider here only the concentration dependence of σ, and assume some type of adsorption to be the origin of this charge (the possibility of ion exchange processes [2] between the membrane and the solution will not be taken into account in our analysis). In order to explain the pore conductivity data for aqueous alkali chloride solutions in track-etched mica membranes, we introduced [8] the Freundlich-type relationship [9]:

$$\sigma(c) = bc^n,\tag{5}$$

where b and n are empirical parameters to be determined in each case. It was suggested [2] that chloride ions adsorb to the pore wall, for the mentioned membranes. Equation (5) holds also for Nuclepore polycarbonate filters, where electrokinetic measurements [5,11] showed that $n \approx 1/3$, and b depended on the electrolyte salt and the membrane studied. If we consider the experimental data of reference [2], we can conclude that (5) accounts for the measured concentration dependence of κ, but it does not satisfactorily reproduce the observed values of v at high bulk concentrations. The main failure of this adsorption isotherm when applied to the streaming potential data comes from the lack of saturation of equation (5) for high electrolyte bulk concentrations (note that (5) predicts "infinite" σ at "infinite" c).

Before to discuss how to modify the adsorption isotherm, it is in order now to summarize briefly some of the previous work in the field. Koh and Anderson [1] wrote a species-specific free energy of adsorption, and added to it an electrostatic term (the adsorbate was in this case heparin, a polyelectrolyte negatively charged). By assuming the nonelectrostatic energy contribution to be constant, they connected the pore wall charge to the pore wall potential through a Boltzmann relationship. Variations of σ with c were explained considering that the heparin adsorption was a function of the electrostatic potential at the pore wall. The agreement between theory and experiment depended very much on the pore sizes, and no saturation was observed at the concentration levels of heparin used there. Nakagaki and Takagi [12] applied a Langmuir-type adsorption

isotherm to the analysis of the affinity membrane potential. The Langmuir adsorption isotherm can be written in our case as

$$\sigma = \sigma_\infty \left[\frac{bc}{1 + bc} \right], \qquad (6)$$

where b is a coefficient, and σ_∞ the saturated amount of the adsorbed pore wall charge density.

Although it is clear that this type of isotherm leads to the observed saturation for σ at large values of c, we have found that it does not reproduce the experimental behaviour of κ and v at small c, which can be satisfactorily described by (5). More recently, Pintauro and Verbrugge [3] have included the specific adsorption of pore-electrolyte species onto the pore-surface fixed-charge sites by adding an adsorption term to the fixed charge site density on the membrane matrix. (This charge density is supposed to be different from zero in their model.) They used a Frumkin isotherm, which for small values of the adsorbed species concentration approaches the previously discussed Langmuir isotherm.

Taking into account the above facts, it is clear that the required adsorption isotherm should give both, the saturation for σ at high c, as well as a relationship similar to that of equation (5) at low values of c. This can be accomplished by modifying (5) in the form [13]:

$$\sigma = \sigma_\infty \left[\frac{bc^n}{1 + bc^n} \right] = \sigma_\infty \left[\frac{B(a/\lambda)^N}{1 + B(a/\lambda)^N} \right], \qquad (7)$$

which approaches the Freundlich isotherm for small values of c, and the Langmuir one for high values of c. (In writting equation (7), equation (2) applied to the bulk solution has been considered). The adsorption isotherm of equation (7) was first proposed by Sips [13] in an attempt to calculate the distribution of the adsorption energies of the sites of a catalyst surface when the adsorption isotherm is known. The isotherm represents a quasi-normal distribution of binding energies centered at the average energy, and gives the Langmuir isotherm as a limiting case when all the sites have the same adsorption energy. Equation (7) is expected to account for the chloride ions adsorption to the pore wall [2]. It seems necessary to point out that this equation involves three free parameters (σ_∞, B, N) rather than two. However, it must be borne in mind that we are going to study the validity of (7) for describing both κ and v over a wide range [2] of bulk concentration values ($10^{-4} < c < 10^{-1}$ M). Hence, an agreement between theory and experiment could support the validity of an adsorption isotherm like that of (7).

C. Pore conductivity

The pore conductivity is an electrokinetic parameter that can be readily calculated since it depends only on the phenomenological coefficient

L_{11} ($\kappa = -L_{11}$, see [2] for details). The final expression is [8]:

$$\kappa = \kappa_b \left[1 - \frac{D_+ - D_-}{D_+ + D_-} \frac{2Fa\sigma}{\varepsilon RT} \frac{1}{q^2} \right] + \frac{\sigma^2}{\eta} \left[1 + Q \left(\frac{2}{q} - Q \right) \right].$$

$$\kappa_b \equiv \frac{\varepsilon (D_+ + D_-) q^2}{2 a^2}, \quad q \equiv \frac{a}{\lambda}, \quad Q \equiv \frac{I_0(q)}{I_1(q)},$$ (8)

where a binary $1:1$ electrolyte has been considered. In equation (8), D_+ and D_- are the ion diffusion coefficients, η is the solvent viscosity, and κ_b is the bulk electrolyte conductivity (which is the limit of κ when $(a/\lambda) \to \infty$). Equation (8) is expected to apply only for $(a/\lambda) \gg 1$.

For $(a/\lambda) \lesssim 1$, equation (3) leads to the pore conductivity [8]:

$$\kappa = - \left\{ \frac{2FD_+\sigma}{aRT} + \frac{\sigma^2}{\eta} \frac{1}{p} \left[1 + \frac{\ln(1-p)}{p} \right] \right\},$$ (9)

where p has been defined in (4). We have shown [8], that each one of equations (8)–(9) agrees quite well with the experimental data from Ref. [2] in their respective ranges of applicability when σ is assumed to be given by (5).

D. Streaming potential

The streaming potential can be expressed in terms of phenomenological coefficients L_{11} and L_{13}. Indeed, $v = -L_{13}/L_{11}$, where L_{13} is [2]:

$$L_{13} \equiv \frac{\varepsilon RT}{F\eta} \left[\psi(1) - 2 \int_0^1 \psi(\zeta) \zeta \, d\zeta \right], \quad \psi \equiv (F/RT)\Psi, \quad \zeta \equiv r/a. \quad (10)$$

Evaluating in each case the integral of (10) with the help of equations (1) and (3), we obtain:

$$v = - \left[\frac{\sigma a}{\eta} \frac{1}{q} \left(\frac{2}{q} - Q \right) \right] \bigg/ \kappa,$$ (11)

for $(a/\lambda) \gg 1$, and

$$v = \frac{2\varepsilon RT}{F\eta} \left[1 - \left(1 - \frac{1}{p} \right) \ln(1-p) \right] \bigg/ \kappa,$$ (12)

for $(a/\lambda) \lesssim 1$. Note that the κ's in (11) and (12) are those of (8) and (9), respectively.

Likewise, the pore wall charge density σ appearing in equations (8)–(12) is that

of (7). Equation (11) gives the well-known Helmholtz result [14], $v = \sigma\lambda/\eta\kappa_b$, in the limit $(a/\lambda) \to \infty$.

3. Results

The continuous curves in Figures 1 and 2 refer to the pore conductivity and the streaming potential values vs. (a/λ). They have been obtained from equations (8)–(9) and (11)–(12), respectively. The circles represent the experimental data taken from [2]. The theoretical curves consider the respective infinite dilution values for the ion diffusion coefficients D_+ and D_-, and the bulk solvent viscosity for η, the dielectric constant being that resulting from the limiting equivalent conductance. Parameters σ_∞, B and N in (7) have been obtained by fitting the theoretical expressions (equations (8)–(9) and (11)–(12)) to the experimental data. This fitting gives $\sigma_\infty = -2.4 \cdot 10^{-2}\,\text{C}/\text{m}^2$, $B = 0.51$ and $N = 0.88$ for the electrolyte system considered (KCl) in a membrane with pore radius $a = 103\,\text{Å}$ [2]. Figure 3 gives the pore wall charge vs. (a/λ) according to (7) with the given parameters.
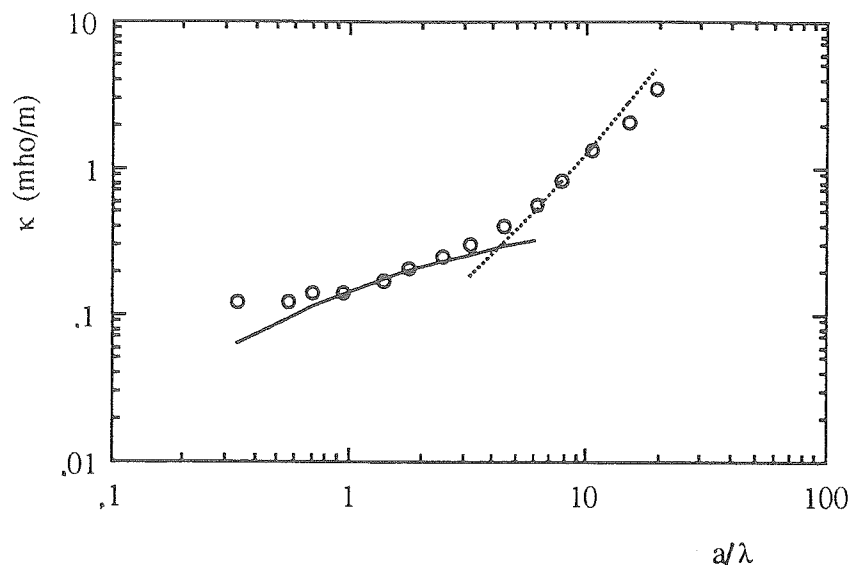

Fig. 1: Pore conductivity vs. (a/λ). The circles are experimental data from Ref. [2]. The continuous line result from equation (9) in the text and the dotted one from equation (8).

Consider first the pore conductivity values. The limiting case of high bulk concentrations (which correspond to high (a/λ) values) leads to $\kappa \approx \kappa_b$, while those of low (a/λ) values give pore conductivities much greater than those corresponding to the κ_b ones at low concentrations. (In this limit the excess of cations within the pore enhances the ability to carry electric current, which gives a pore conductivity much greater than that of a bulk fluid with the same electrolyte concentration.) On the other hand, it can be recognized that the streaming potential values are approximately described by the Helmholtz

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equation at high (a/λ) ratios. The streaming potential increases when (a/λ) gets lower: it is clear that for $(a/\lambda) \leq 1$, the electric double layer fills in all the pore and thus the electrokinetic effects become very noticeable. All these experimental trends are approximately represented by the theoretical curves within their respective ranges of applicability. The agreement between theory and experiment can be considered as reasonable, if one takes into account the number of approximations involved in the model, as well as the fact that, for the sake of simplicity, we are employing two limiting forms of the $P - B$ equation.
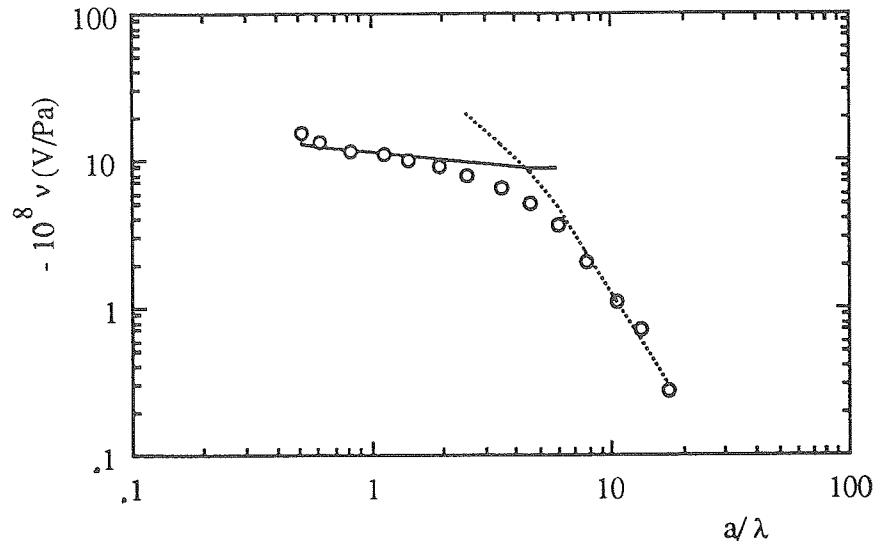
Fig. 2: Streaming potential vs. (a/λ). The circles are experimental data from Ref. [2]. The continuous line result from equation (12) in the text and the dotted one from equation (11).
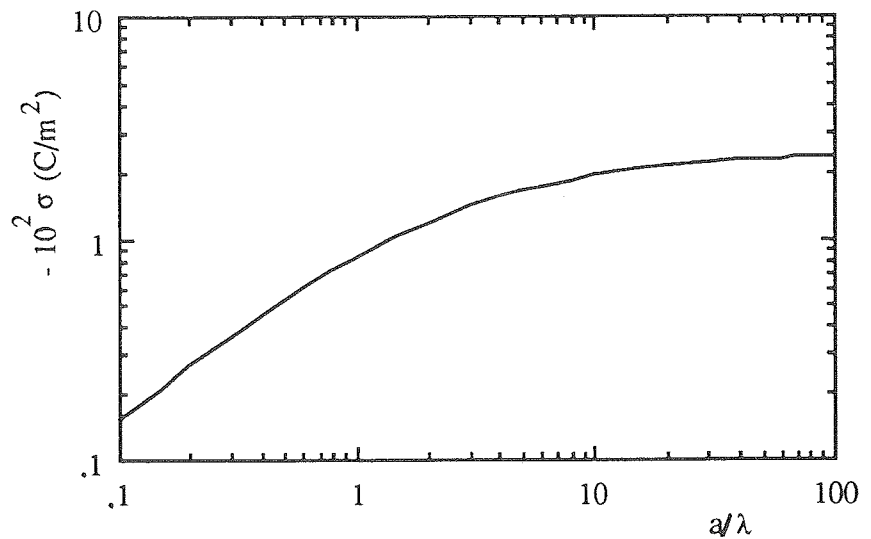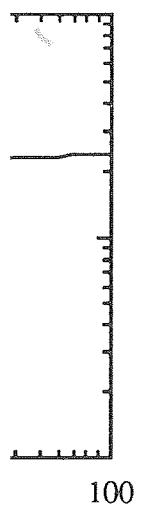
Fig. 3: Pore wall charge density derived from equation (7) in the bulk electrolyte concentration range considered. Fitting parameters take the values: $\sigma_{\infty} = -0.024 \, \mathrm{C/m^2}$, $B = 0.51$ and $N = 0.88$.

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4. Discussion

Previous studies [1, 2, 7] of the capillary model for charged membranes have considered numerical solutions of the problem where no particular dependence of the charge density σ was assumed. It is difficult to introduce such a dependence due to the high number of phenomena affecting this pore wall charge. Here we have tried to take the model a step further, and show that a relatively simple relationship of σ on the bulk concentration c together with the analytical solutions corresponding to two limiting cases of the $P - B$ equation, can give a reasonable first approximation to the measured κ and v values [2] over the concentration range 10^{-4} to 10^{-1} M. The incorporation of relationships similar to those of equations (5) and (7) for σ in the more complete, exact numerical treatments by Westermann-Clark and Anderson [2], and Martínez *et al.* [7], can significantly improve the results, though it is sometimes the case [15] that important information can be obtained without performing the rigorous integration of the formidable non-linear differential equations ruling the problem.

In order to incorporate the Freundlich isotherm characteristics for small values of c as well as the Langmuir isotherm ones for high values of c, a "patched" Freundlich-type relationship has been introduced. Bearing in mind the three free parameters involved in (7) as well as the model assumptions introduced, it may be difficult to decide whether (7) is a good first approximation to the adsorption problem or simply deviations from experiment behave in such a way that a particular choice of the fitting parameters can describe in some average way the observed phenomena. On the other hand, it is clear that the adsorption isotherms considered for track-etched mica [2] (equations (5) and (7)) and Nuclepore [5, 7] (equation (5)) membranes should not necessarily apply to other membranes with adsorbed pore charge. In this context, we must mention that other mechanisms in addition to ion adsorption can influence the pore charge (ion exchange might be one of the origins for the pore wall charge of the mica membranes; see [2] and references therein).

However, the following points should be emphasized: i) Equation (7) has a physical basis (the suggested adsorption phenomena [2, 4, 7]); ii) this equation gives good results over a relatively wide region of κ and σ values (note that the experimental data for κ and v in [2] were satisfactorily described only after introducing a ratio of $\sigma(\max)/\sigma(\min) = 2.5$ between the maximum and minimum values of the free parameter σ); and iii) equation (7) has not been introduced previously, as far as we know, in capillary models for charged membranes. Also, it is worth noting that (7) has passed a critical test, which is that of the validity of the same σ values to describe both the κ and v observed values. In [1], the pore wall charge values obtained from conductivity and electroosmosis measurements at identical physical conditions did not agree and in some cases differed by a factor of five. (It has been pointed out [2] that this fact may be due to the particular polyelectrolyte employed (heparin) and the fact that the measurements were done on two different membranes.)

Let us note finally a question of considerable practical importance. There exist a number of experimental procedures to characterize the pore wall charge. Koh and Anderson employed enhanced conduction and electroosmosis experiments [1]. Martínez *et al.* used the pore permeability measurements and the concentration potential ones [7]. Westermann-Clark and Anderson [2] analysed the pore conductivity and the streaming potential values. As mentioned by these authors, there are good reasons to use the conductivity data to determine the absolute value of σ (the sign of σ must be ascertained from the streaming potential). However, the pore conductivity data are not sensitive to σ at high concentrations, so that in order to decide if there exists saturation in the adsorbed pore wall charge and determine the value of σ_∞, the streaming potential measurements should be employed: the magnitude of v is very sensitive to σ at high (a/λ), [2].

Acknowledgements

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J. Non-Equilib. Thermodyn., Vol. 16, 1991, No. 3